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C. Project NY 450 004-4 Technical Memorandum M-111

COMPATIBILITY OF SOME UNDERWATER COATING SYSTEMS WITH CATHODIC PROTECTION - A PRELIMINARY STUDY

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Project NY 450 004-4
Technical Memorandum M-111

COMPATIBILITY OF SOME UNDERWATER COATING SYSTEMS WITH CATHODIC PROTECTION - A PRELIMINARY STUDY

10 February 1956

E. R. Streed

### SUMMARY

Use by the Bureau of Yards and Docks of cathodic protection, often in conjunction with a coating system, to combat the corrosion of submerged areas of floating and stationary structures has increased significantly in recent years.

A total of 21 coating systems, including a variety of proprietary and some standard Navy systems, were applied to test panels and were studied for one year using an impressed-current cathodic protection system. The performance of these coating systems relative to adhesion, blistering, fouling, and current requirements is described.

Of the Navy systems studied, Formula No. 15 hot plastic antifouling and Formula No. 113 vinylidene chloride (Saran) exhibited superior performance. The Navy systems using Formula No. 14 anticorrosive showed less electrolytic resistance than the synthetic resin coating systems. Electrolytic resistance of a coating system though it is desirable may not be as important as the deterioration-resistant properties of a coating system when subjected to cathodic currents.

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### INTRODUCTION

Compatibility of cathodic protection and paint coatings for corrosion protection of steel structures submerged in water has been the subject of several investigations. A review of some of these investigations 1-7 revealed that a variety of conditions and coatings were used depending upon the objective of the study. The role of electro-osmosis and the importance of alkali resistance and permeability of a coating system in use with cathodic protection has been emphasized. 1 The antifouling properties of ship bottom paints subjected to relatively high cathodic potentials have been studied and the value of anticorrosive undercoatings in minimizing inactivation (susceptibility to fouling) and accelerated corrosion of the steel has been demonstrated. 2 A two-year test of a vinyl system in sea water at a closely controlled potential of 840 millivolts with respect to a silver chloride reference electrode gave superior performance according to one report. 3 In another study the rate of paint deterioration was roughly proportional to the amount of current and the resultant polarization. <sup>4</sup> The formulation of a coating system possessing good adhesion, high alkali resistance, relatively low electrical resistance, and a porous structure to permit outward diffusion of cathodic products has been suggested. 5

In the references cited it was concluded that high electrolytic resistance coatings were desirable to limit the magnitude of the cathodic current. In addition, a high degree of alkali resistance minimized accelerated coating deterioration. Film thickness also was a significant factor. As expected, the thicker coatings were less affected by the application of cathodic protection. In every instance, close control of the cathodic potential was emphasized. A potential value, very close to the open circuit potential of steel in sea water, eliminated pitting and reduced surface corrosion to negligible amounts without appreciably affecting most paint systems. Effects resulting from the imposition of negative potential values of 1.0 volt or greater with respect to a copper sulfate cell varied widely with the different coating systems. Practically all coatings

showed some deterioration after protection for periods up to two years at the higher potentials. The studies served to point out that the deterioration involved is the result of many factors which were not evaluated individually, and it was concluded that more extensive studies are needed.

In view of these somewhat specialized studies and the increasing use of cathodic protection, preliminary evaluation of 21 coating systems in conjunction with cathodic protection was initiated. The objective of this study was to determine the behavior of certain standard Navy underwater coatings and to evaluate them on the basis of blistering, adhesion, fouling, and current requirements. In addition, some special proprietary coatings were included in the study for comparison.

This preliminary study was performed under Project NY 450 004-4 Corrosion Prevention and Special Coatings, Subtask 4, Cathodic Protection. The objective of the subtask is to develop satisfactory methods of employing cathodic protection to prevent or inhibit corrosion of submersed or buried metal surfaces.

### THEORETICAL CONSIDERATIONS

The electrochemical concept of the corrosion of a metal immersed in sea water implies that corrosion is the result of ionic current flow between the anodic and cathodic areas of the exposed metal. Thus, the mitigation of electrolytic corrosion can be achieved by retarding either the cathodic or anodic electrolytic reactions or by increasing the electrolytic resistance between these areas. Excellent descriptions of the mechanism of paint protection and cathodic protection individually have been presented elsewhere. A brief discussion of the corrosion process and the roles of paint and cathodic protection is presented to point out some problems associated with the simultaneous use of both.

It has been found that most paint films are so permeable to water and oxygen that they cannot inhibit corrosion by excluding them from the surface of the metal. <sup>8</sup> This penetration of the paint film is due to electrokinetic phenomena occurring along minute capillaries existing in the film. Osmotic diffusion derived from a potential gradient existing across paint films has been

reported. <sup>10</sup> Other factors such as electrophoresis and the seta potential have been suggerted as contributors to the ionic transfer rate. <sup>11</sup> These factors are dependent upon the pigment type and amount, vehicle type, and the composition of the electrolyte.

Thus, it can be assumed that the rate of the cathodic reactions is primarily dependent upon the removal of the reaction products. The most common cathodic reactions are:

- 1.  $0_2 + 2H_20 + 4e > 4(0H)^-$  (reduction of molecular oxygen)
- 2.  $2H^+ + 2e \rightarrow 2H \rightarrow H_2$  (reduction of hydrogen ions)
- 3.  $Fe^{++} + e \rightarrow Fe^{++}$  (reduction of ferric ions)

The cathodic reactions produce hydrogen which can result in hydrogen blistering or hydroxyl ions which in sea water are readily converted to sodium hydroxide and can result in alkaline blistering, undercutting, and loss of adhesion. With the introduction of cathodic currents and resultant higher negative potentials the possibility of accelerated film deterioration is inevitable unless the potential is closely controlled. It is apparent, therefore, that the properties of a coating which enhance its cathodic protective ability may also contribute to its deterioration by trapping or reacting with corrosion products formed at the coating-metal interface.

The primary anodic reaction  $4Fe \rightarrow 4Fe^{++} + 8e$  can be controlled by: (1) making the steel more negative by furnishing electrons to the anodic area, or (2) passivation with an impervious film such as an oxide coating. The first method is the technique employed by cathodic protection and can be accomplished with a suitable metallic pigmented coating or an external current supply.

The electrical resistance of a coating system has been found to give good correlation with service life. <sup>10</sup> The magnitude and distribution of cathodic currents is directly related to the resistance properties of a paint film.

A sea water environment and the additional requirement that most Naval floating equipment remain free of fouling add to the difficulties of obtaining an optimum coating system. Experience

has shown that the coating systems presently in use will not completely eliminate corrosion over extended periods. The utilization of a cathodic protection system without coatings is capable of adequate corrosion protection; however, the magnitude of the current requirements demands an extensive current distribution system. Therefore, cathodic protection and protective coatings are not necessarily alternative methods of protecting an immersed surface; in many cases a combination of the two methods is the most economical means of providing corrosion resistance.

The selection of the coating system may be dependent upon whether the coating or cathodic protection is determined to be the prime agent of corrosion mitigation. For instance, certain types of floating equipment must be drydocked periodically for reasons other than replacement of the paint system. If a good, properly applied coating system will perform satisfactorily for two to three years, the addition of cathodic protection during this period is not necessary and could cause physical damage to the coating if not carefully controlled. When it is suspected or determined that the coating has deteriorated sufficiently to permit significant corrosion to occur before a scheduled reconditioning can be performed, cathodic protection can be employed to effectively retard the corroding action. In this policing or stopgap role, the economies of cathodic protection must be justified for each particular situation.

On the other hand, if cathodic protection is selected to play the major role in combatting corrosion of a structure, the application of a coating system is made to reduce the initial and continuing expense of supplying an adequate current. The prime requisite of the coating is to remain intact and provide as much electrolytic resistance as possible. The coating would not be replaced until it had deteriorated to the extent that the current requirements exceeded the design capabilities of the cathodic protection system. Justification of this use of cathodic protection would be based upon the savings effected by the extension of the reconditioning period versus the total cost of the cathodic protection system.

The application of cathodic protection to permanently installed structures which are inaccessible for maintenance painting should be justified on the basis of installation and maintenance costs of the system versus costs associated with replacement of the structure.

### DESCRIPTION OF TEST FACILITY

The local harbor test site was chosen over a laboratory installation to better duplicate a typical service environment. Because of its permanence and range of control, an impressed current system using a graphite anode was employed. A circulartype floating suspension for the panels was designed to permit mounting of a 3-inch by 60-inch anode in the center as shown in Figure 1. Test panels 6 feet in length by 4 inches wide and 1/4 inch thick were mounted on individual 3/4-inch thick bakelite insulating blocks which were bolted to a metal ring support. The symmetry of the design insured even current distribution over the 5-foot submerged portion of the panel. Cathodic currents were measured and controlled individually by the control system shown in Figure 2.

Potentiometer-type potential measurements were made at an external terminal box located on the dock adjacent to the float. All potential measurements were made with a copper sulfate half cell located near the center of the float. An optimum negative potential of 0.850 volts was desired. Maintenance of this potential was difficult to achieve because of varying ambient conditions. The test facility was located in the harbor entrance channel and therefore experienced varying degrees of vertical movement because of the wave action produced by the passage of vessels through the channel. This movement, tidal currents, and changes in weather conditions resulted in intermittent depolarization of the panels. Because of the desire to duplicate service conditions and potentials as much as possible the potential was considered satisfactory if maintained within the 0.800- to 1.00-volt range. After initial equilibrium values were reached, potentials were measured on a weekly schedule. Typical potential values for the year are presented in Figures 3a and 3b for the panels, Nos. 1, 4, 6, 7, 8, 9, 15, 16 and 17. Figure 3b also presents similar graphs for the aluminum- and zinc-coated panels (flame sprayed), Nos. 20 and 21. The potential of several of the panels, not receiving cathodic protection, was found to vary between 550 and 690 millivolts. No correlation was noted between these potentials. and the amount of corrosion or paint deterioration.

The selection of coatings was based upon the Bureau of Yards and Docks' suggestions of standard Navy systems presently in use on underwater structures 11 and proprietary coating systems showing the most promise in existing Laboratory sea water immersion tests. The number of coatings was limited due to the size of the test facility and control method necessary for the cathodic profection system. Therefore, this preliminary study incorporated as broad a selection of coatings as possible but only one panel of each. In most instances, duplicate panels were prepared from the same coating material and were immersed in a similar environment but were not subjected to cathodic currents.

Most coatings were applied, except as noted in Table I, under Laboratory supervision using instructions provided by the supplier. Two panels coated with Formula No. 15 hot plastic were prepared for comparison data. . Panel No. 8 was prepared by using the appropriate spray equipment. Panel No. 12 was prepared by flowing the hot plastic on the panel and smoothing the coating to the desired thickness with a heated rod. As the study progressed duplicate panels were prepared for the coatings, Nos. 18 and 22, which had initially required abnormally large currents. Two vinyl systems were also added later in the study. Table I lists the coating systems, a brief identification of each, and the average thickness. Each panel was coated on both sides and scribe marks were cut diagonally across one side to accelerate blistering and adhesion effects. The panels were placed on the support with the scribed side facing the anode. The panels were removed and inspected after 6-, 9-, and 12-month exposure periods.

### CURRENT DATA

The average impressed current for the first and twelfth month for the various panels is tabulated in Table I. Variations in the width of the scribe mark, caused by chipping of brittle coatings or healing by the softer coatings, restrict the value of this data for precise estimates of current density requirements of unscribed panels. However, a comparison of the impressed current values provides an indication of the relative electrolytic resistance of the coatings.

TABLE I. A tabulation of the description and

Panel		Coatings		Average current (ma)		Rating	Comments
No.	Туре	System	thickness (mils)	1st month	12th month		Comments
I	epoxy resin	red lead epoxy primer; amine catalyzed epoxy resin	31/2	0.206	0.470	7	high electrical resistance, susceptible to extensive blistering, good adhesion
2	phenolic resin	red lead with 40% mica primer; 100% solids modified phenolic resin	16	0.086	0.103	9	high electrical resistance, slight blistering on scribe side, excellent adhesion
3*	Formula No. 105 cold plastic AF	Formula No. 117 wash primer; Formula No. 14 AC Formula No. 105	1/4 3 71/4	1.59	25.3	2	medium blistering over whole panel causing cracking and loss of complete system in 25% of are
4•	coal tar	cold primer hot enamel 34Yb	40 60	0.255	3.57	8	good electrical, alkali, and blistering resistance; costing brittle and easily chipped
5	inorganic zinc	zinc pigmented inorganic silicate vehicle	3	0.0	4.33	В	inherent protection decreased to permit superficial rusting after 5 months; poor electrical resistance, excellent bonding to metal
<b>ٽ</b>	pomnés No. 113 Saran	Formula No. 117 wash primer; vinylidene chloride acrylonitrile copolymer	% 5%	0.219	0.143	9	high electrical resistance; no alkeli or blistering effects, fair adnesson to wash prime
7	furan resin	red lead, iron oxide chromate primer; nonpiastici>>d furan resin	11/4	0.228	1.11	7	high electrical resistance; medium blistering and loss of adhesion of topcoat
8*	Formula No. 15 hot plastic AF	Formula No. 117 wash Formula No. 14 AC Formula No. 15 HP	3½ 60	0.530	5.32	8	fair electrical resistance; no alkali or blistering effects; coating brittle with only fair adhesion to primer; excellent antifouling properties
90	Formula No. 145 cold plastic AF	Formula No. 117 Formula No. 14 AC Formula No. 145	1½ 3 8	2.30	12.8	1	poor electrical resistance; flaking causing loss of topcoat in 75% of area; loss of primer in 15%
12	Formula No. 15 hot plastic AF	Formula No. 117 Formula No. 14 AC Formula No. 15 HP	1/3 3 33	0.243	2.91	9	good electrical resistance; no alkali or blistering effects; excellent antifouling properties
13	vinyl acrylic lacquer	Formula No. 117 vinyl acrylic lacquer	½ 6	0.163	3.67	6	high electrical resistance but susceptible to large blistering and ultimate peeling
14	oil-modified alkyd resin	red lead pigmented alkyd resin, oil-modified	51%	0.393	17.7	3	fair electrical resistance; poor alkali resistance causing softening and flaking

<sup>\*</sup>Applied at Long Beach Naval Shipyard.



id performance of the coating systems studied.

ot plastic

AF Antifouling

Panel	No.	Coatings	Average thickness	Average current (ma)		Dari-	
No.	Туре	System	(mils)	1st month	12th month	Rating	Comments
15	zinc pigmented	86% zinc pigmented polymerized polystyrene	4½	0.0	2.57	8	inherent protection decreased to permit superficis rusting after 1st month; fair electrical resistance excellent bonding to metal
16	vinyl chloride	Formula No. 117 12% pigmented polyvinyl chloride	½ 5½	0.231	1.66	6	high electrical resistance; large blisters on 10% of area; fair adhesion to wash prime
17	chlorinated rubber	wash primer red lead pigmented primer chlorinated rubber	3 4½	0.122	0.670	7	high electrical resistance; slight undercutting along scribe; topcoat flaking but primer good
16	neoprene	special primer, catalyzed neoprene	2 8	10.0	7.24	5	poor electrical resistance; medium blistering and flaking of topcoat
19	Cu, CuO, Zn pigmented resin (unknown) AF	Zn chromate anti- corrosive mica pigmented insulator Cu, CuO, Zn pigmented resin	1.0 2.0 3.0	0.717	14.36	4	fair electrical resistance; medium blistering and cracking causing loss of entire system over 25% o area
20	Zn metai spray	No. 25 carbon steel Zn flame-sprayed wire	6	0.0	0.0	9	protective ability still excellent, excellent bonding to metal
21	aluminum metal spray	No. 25 carbon steel Al flame-sprayed wire	11/2	0.0	0.0	9	medium surface blistering but inherent protective ability still good, excellent bonding to metal
22	Formula No. 129 vinyl AF	Formula No. 117 Formula No. 119 Formula No. 129	½ 2 3	8.0	87.4	2	no blistering or alkali effects; excessive current requirements apparently due to Cu pigmentation
23	coal tar	34Yb cold applied coal tar	52	0.25	2.82	8	good electrical, alkali, and blistering resistance;
24	Formula No. 129 vinyl AF	Formula No. 117 Formula No. 119 Formula No. 129	½ 2 5	0.54	2.34 (9 mo.)	not rated	unscribed with improved current characteristics; no alkali or blistering effects
28	neoprene	neopresse primer, catalyzed neoprene	1 3 to 20	3.04	2.46 (4 mo.)	not rated	topcoat thickness varied to study deterioration rates; no visual effects after 4 months; fair electrical resistance
29	sluminum vinyl	Formula No. 117 Formula No. 119 Al pigmented vinyl lacquer	2 3	0.11	0.15 (5 mo.)	not rated	high electrical resistance; no blistering or alkali effects detected after 5 months
30	vinyl mastic	Formula No. 117 vinyl primer vinyl mastic	½ 1½ 7	0.26	0.53 (5 mo.)	not rated	high electrical resistance; some blistering along scribe, good adhesion



A classification of the coatings into three groups based on the initial impressed current is made in Table II. Those receiving currents below 0.30 milliamperes, Group A, are considered to exhibit good electrolytic resistance; those receiving between 0.30 and 1.0 milliamperes, Group B, are considered to exhibit fair resistance; and those receiving more than 1.0 milliampere, Group C, are considered to exhibit poor resistance. The relatively high initial currents required by the Formulas Nos. 105, 145, and 129 coatings are attributed to either insufficient primer thickness or; inferior insulating properties of the system. Although the same primer system was used, current requirements for Formula No. 15 hot plastic were apparently less because of the greater topcoat thickness. On the basis of the data presented in Table II, the Group A coatings would be expected to perform better when not a subjected to cathodic currents. Group A coatings may not be the best choice when used with cathodic protection because electrolytic insulation is not the only factor to be considered.

A similar classification based on average impressed currents during the twelfth month is presented in Table III. The current ranges in Table III have been arbitrarily increased by a factor of 4 to account for deterioration. The Group A coatings listed in Table III have exhibited superior electrolytic insulating properties, prime requisite of a cathodic protection coating. The current demands of the vinylidene chloride (Saran) have decreased even after one year of exposure indicating that the initial imperfections in this coating had become coated with cathodic deposits without damaging the coating. The epoxy, furan, chlorinated rubber, and phenolic coatings have been affected by the cathodic currents but the damage has not progressed sufficiently to cause a serious loss of electrolytic resistance.

The difference in current requirements between the two Formula No. 15 hot plastic panels is apparently due to the method of application of the coating. The No. 12 panel was prepared as described under COATING AND PREPARATION OF PANELS and even though the average thickness was much less, the flowing and smoothing of the coating apparently reduced the number of imperfections in the topcoat.

No external current has been applied to the aluminum- or zinc-coated panels (flame sprayed) because the natural protection

afforded by the anodic metal has maintained an adequate potential. The two sinc-pigmented coatings did not receive external current until the potential of the panel had decreased to 0.750 volts. It is interesting to note that although these coatings had relatively low initial electrolytic resistance, the additional current required to maintain the desired potential is of approximately the same magnitude as coatings exhibiting much higher initial electrolytic resistance. This apparent increase in electrical resistance is attributed to either the formation of insulating products on the coating surface or the back voltage created by the electropositive action of the zinc.

The exceptionally large current required by Formula No. 129 (Panel No. 22) is attributed to the metallic copper pigmentation. A duplicate unscribed panel (No. 24) exposed for six months has required a much lower current. Evidently metallic copper leached out of the topcoat and deposited in the scribed area. This behavior of a metallic copper pigmented coating was also demonstrated to a smaller degree by Panel No. 19. A study of the mechanism of accelerated corrosion due to certain toxic pigments has been reported in the literature. 12

The poor electrolytic resistance of the neoprene coated panel No. 18 was surprising and no ready explanation can be given based on the known electrical properties of this material. A duplicate panel (No. 28) required less current but the current magnitude was still approximately ten times larger than that required for some of the synthetic resin systems.

### PERFORMANCE OF COATINGS

Of the standard Navy coatings investigated, Formula No. 15 hot plastic system (panels No. 8 and No. 12) and the 34Yb coal tar coatings (panels No. 4 and No. 23) performed without visual signs of excessive deterioration. Photographs of two of these coatings are shown in Figure 4. The Formula No. 145 cold plastic coating both with and without cathodic protection failed (see Figure 4). The topcoat had flaked off in 75 per cent of the scribed side area of the cathodically protected panel. Although the primer remained in place over 90 per cent of the panel, it became soft and was easily removed with abrasion. Slight rusting had occurred along the scribe marks; however, the amount was negligible compared

TABLE II. Classification of coatings based upon the average impressed current during the first month of exposure.

	Group A			Group B			Group C	
Panel	Coating	Current (ma)	Panel	Coating	Current (ma)	Panel	Conting	Current (ma)
1	ероху	0.206	8	Formula No. 15	0.530	3	Formula No. 105	1.59
2	phenolic	0.086	14	oil-modified	0.393	9	Formula No. 145	2.30
4	34Yb hot coal	0.255		alkyd resin		18	neoprene	10.0
	tar		19	Cu pigmented AF	0.717	22	Formula No. 129	8.0
5	Zn pigmented inorganic	0.0		AF				
6	Saran	0.219				]		
7	furan	0.228						
12	Formula No. 15	0.243				]		
13	vinyl acrylic	0.163				}		
15	Zn pigmented polystyrene	0.0						
16	vinyl chloride	0.231						i
17	chlorinated rubber	0.122						
23	34Yb cold coal tar	0.250			п			

TABLE III. Classification of coatings based upon the average impressed current during the twelfth month of exposure.

	Group A			Group B		Group C		
Panel	Coating	Current (ma)	Panel	Coating	Current (ma)	Panel	Coating	Current (ma)
1	epoxy	0.470	4	34Yb hot coal	3 - 57	3	Formula No. 105	25.3
2 6	phenolic Saran	0.103 0.143	12	formula No. 15	2.91	5	Zn pigmented inorganic	4.33
7	furan	1.11	13	vinyl acrylic	3.67	8	Formula No. 15	5.32
17	chlorinated rubber	0.670	15 16	Zn pigmented polystyrene vinyl chloride	2.57	9 14	Formula No. 145 oil-modified alkyd	12.78 17.7
			23	34Yb cold coal	2.82	18	neoprene	7.24
				tar		19	Cu pigmented AF	14.36
						22	Formula No. 129	87.4

to the rusting and pitting of the panel without cathodic protection. Poor performance of both Formula No. 145 and Formula No. 105 has been previously reported when maintained at potentials above 0.80 volts negative with respect to a saturated calomel reference (approximately 0.875 volts to copper sulfate). <sup>13</sup> Similar lack of adhesion between the topcoat and primer was experienced to a smaller degree with the chlorinated rubber and the neoprene. These coatings are shown in Figure 5.

The Formula No. 129, antifouling vinyl, panel No. 22, Figure 5, does not visually show signs of deterioration. However, rusting and slight pitting along the scribe mark are prevalent. Again the extent of corrosion is less severe than that which occurred on the panel that was not subjected to cathodic protection. Of the synthetic resin coatings tested, vinylidene chloride (Saran), panel No. 6, Figure 5, performed the most satisfactorily. Rather weak adhesion was obtained between the coating and the Formula No. 117 wash prime but this was attributed to the use of wash prime with this coating rather than to cathodic effects.

The magnitude of blistering of two of the proprietary coatings that were subjected to cathodic protection as compared with those same coatings that were not cathodically protected is illustrated in Figure 6. In addition to blistering the furan resin showed weak adhesion between the primer and the metal surface. No rusting and no pitting were visible under the blisters or along the scribe marks. Unprotected panels with these coatings are in excellent condition. Two additional vinyl coatings, panels No. 29 and No. 30, under test for 5 months, indicate the great difference in the performance of a coating system based on the same resin type. The aluminum pigmented vinyl has shown no tendency to blister but the vinyl mastic has been affected along the scribe marks as illustrated in Figure 7.

The influence of current density on a system susceptible to blistering is illustrated by the epoxy coating, panel No. 1, Figure 8. The coated panel without cathodic protection although suffering only slightly, shows a natural tendency to blister. The unscribed side of the cathodically protected panel, facing toward the outside of the float, was shielded from the anode and therefore subjected to lower current densities. The scribed side, facing the anode, experienced the greatest effect as evidenced by the greater number and size of the blisters.

The blistering susceptibility of epoxy and epoxy-phenolic resin coatings found promising for use in hot water tanks has been reported. 14

According to the report, <sup>14</sup> studies of the variation in pigmentation indicated that epoxy-phenolic coatings pigmented between 20 and 40 per cent with TiO<sub>2</sub> greatly increased the permeability and blistering effects. However, pigmentation below 20 per cent produced high resistance coatings with only slight blistering. The conclusion of this study stated that although blistering does not appreciably affect the electrical resistance of the film, indications are that a complete loss of coating adhesion could occur over an extended exposure time.

The zinc and aluminum coated pahels (flame sprayed),
Nos. 20 and 21 shown in Figure 7, experienced minute surface
blistering but are still in excellent condition. The protected zincpigmented coatings, panel No. 5, are shown in Figure 9. Again
surface blistering occurred particularly on the polystyrene-type
coating. The bright spots on the unprotected panels (see Figure 9)
are the areas where the steel surface has become exposed. Only
slight superficial rusting has occurred in these areas.

Few of the proprietary coatings were pigmented to resist fouling. Of the antifouling coatings, Formula No. 15 hot plastic performed the best. The resistance of the zinc coatings was particularly effective against fauna (animal growth). The 34Yb coal tar coatings accumulated animal growth over approximately 15 per cent of the panel area and permitted types of barnacles to burrow through the coating. In general, little difference in type or amount of fouling was discernible between panels cathodically protected and panels unprotected by cathodic currents.

A rating of the various systems based on their performance with respect to blistering, adhesion, and electrolytic resistance is listed in Table I. Since most of the proprietary coatings were not pigmented for fouling resistance, fouling was not considered in the rating. A rating of 10 denotes excellent and a rating of 0

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signifies complete failure. Blistering was weighted 20 per cent, electrical resistance 30 per cent and adhesion 50 per cent of the total rating factor. Comments pertinent to the performance of each system are also listed to Table Lat-

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### **DISCUSSION OF RESULTS**

The results obtained in a preliminary study of this type should not necessarily eliminate a particular coating type from further study. The influence of variations in type and amount of pigmentation, vehicle type, and thickness of all films comprising a system are significant factors in producing an optimum coating system.

The susceptibility to blistering of most high electrolytic : resistance systems with total film thicknesses of 3 to 6 mils has been demonstrated. Thick film systems, 30 mils and greaters. did not show visual signs of blistering. The synthetic rubber, alkyd resin, and oil modified systems exhibited loss of bonding strength resulting in flaking and peeling condenses and a property of iv for hib bits of

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All systems which included a red lead pigmented primer: evinced good electrolytic resistance and in instances where the topcoat failed, the primer remained in good condition. Those systems which incorporated the Formula No. 14 AC, approximately 3 mile thick, exhibited only fair electrical resistance and when exposed through failure of the topcoat, the anticorrosive became soft. The current required for systems pigmented with metallic copper became excessive regardless of the condition of the conting.

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المناور العي The aluminum and ziac metal (flame sprayed) coatings exhibited good antifouling and corrosion inhibiting properties. No estimate of their service life is possible after one year's exposure. The relatively rapid decrease in the inherent protective abilities of the zinc pigmented coatings resulted in slight surface rusting before the application of external cathodic currents. The open circuit potential of the inorganic zinc coated panel was 708 millivolts after one year's exposure. Because of the high metallic pigmentation of these coatings, ourrent requirements could become excessive after an extended exposure period. Body James & Ber

Conclusions about the expected service life of a particular coating system would only be indicative rather than final after a one year exposure period. Accumulative effects over longer exposure periods could result in complete failure of a system. For a relatively short period, the effects displayed are slight.

### **CONCLUSIONS**

The behavior of 21 coating systems exposed for one year to cathodic potentials normally encountered in manually controlled cathodic protection installations is described. The following conclusions can be made from the studies performed to date.

- 1. Of the standard Navy systems studied, Formula No. 15, hot plastic system, showed superior performance; however, it required more current than most of the proprietary synthetic resin coatings.
- 2. Of the synthetic resin coatings, Formula No. 113, vinylidene chloride (Saran), exhibited exceptionally good electrical resistance and did not visually suffer abnormal deterioration.
- 3. The study described here has substantiated previous investigations reported in the literature illustrating paint degradation effects occurring at a steel cathode immersed in water. Loss of adhesion, blistering and electrolytic resistance have been found to be significant factors in the selection of coatings for use with cathodic protection. The possibility of excessive current requirements for metallic copper pigmented coatings because of breaks in the coating or insufficient insulation by the primer has been demonstrated. Of the desirable coating properties, alkali resistance is considered the most important because it is more closely associated with the loss of adhesion and the possible complete loss of the coating system in a relatively short time. Excessive permeation of a coating is conducive to hydrogen blistering but may not necessarily result in the exposure of the metal surface. Electrolytic resistance is desirable from an economic standpoint; however, even a relatively low electrolytically resistant costing, which would remain intact for the full exposure

period, may be the most economical system by extending reconditioning schedules.

- 4. A cathodic potential level sufficient to retard electrolytic corrosion currents must be continuously controlled to minimize degradation of a complementary coating system. The criterion that the potential of a coated immersed structure should not exceed approximately 1.0 volt negative with respect to a copper sulfate half cell is borne out.
- 5. A comparison of test panels coated with identical systems and exposed in the same environment has illustrated the ability of cathodic protection to eliminate pitting and reduce surface corrosion to negligible amounts.

### RECOMMENDATIONS

The extreme range of results obtained with the limited number and choice of coating systems investigated in this study have shown the need for further research toward development of optimum coatings for use with cathodic protection on steel structures immersed in sea water. Further studies are recommended as follows:

- 1. A systematic study of pigmentation type and amount using the most promising vehicles should be conducted. Formulation should be accurately known and prepared by an impartial party. Variations in thickness should also be considered.
- 2. Three different cathodic potential levels should be investigated with each coating system, i.e., from 0.70 to 0.80, 0.80 to 0.90, and 0.90 to 1.0 volts negative with respect to a copper sulfate half cell. This study would provide data correlating deterioration of a coating with corrosion rate of a metal surface maintained within a specified potential range.
- 3. A record of the required current necessary to maintain the desired potential should be kept. Such data are important to the design and economies of a cathodic protection system. The use of scribed panels is not advocated because of the adverse influence on the validity of cathodic protection current data.

4. A study of the effects of applying cathodic protection to a freshly coated surface as compared to one which has been exposed one to six months is suggested. Most good coatings exhibit a loss in electrolytic resistance after initial submergence followed by an increase to a relatively stable resistance after approximately 30 days. The use of cathodic protection during this "repairing" period may have a deleterious effect on the coating.

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### REFERENCES

- Eickhoff, A. J. and Hawke, D. J., "Some Factors Affecting Paint Performance on Cathodically Protected Steel," <u>Corrosion</u>, vol. 7, February 1951, p. 70.
- Devoluy, R. P., "Behavior of Shipbottom Paints Subjected to Cathodic Protection - A Preliminary Study," <u>Corrosion</u>, vol. 9, January 1953, p. 2.
- 3. Greenblatt, J. H., "Sea Water Immersion Trials of Protective Coatings," Corrosion, vol. 10, March 1954, p. 95.
- 4. Crosby, W. L., "The Use of Cathodic Protection in Conjunction With Paint Coatings, "Corrosion, vol. 6, November 1950, p. 383.
- 5. Sudrabin, L. P., "The Use of Cathodic Protection With Conventional Paint Systems," Paint and Varnish Production Manager, vol. 41, May 1951, pp. 8 and 27.
- Sudrabin, L. P., Le Febore, F. J., Hawke, D. L. and Eickhoff,
   A. J., "Some Effects of Cathodic Protection on Conventional Paints," <u>Corrosion</u>, vol. 10, March 1954, p. 95.
- 7. Oxley, G. W., "Coatings for Protection of Steel in Water,"

  Paint and Varnish Production Manager, vol. 41, March 1951, p. 10.
- 8. Mayne, J. E. O., "How Paints Prevent Corrosion," <u>Corrosion</u>
  <u>Technology</u>, vol. 1, October 1954, p. 286.
- 9. Brown, R. H. and English, G. C., "Electrochemical Principles of Cathodic Protection," <u>Cathodic Protection</u>, A <u>Symposium</u> (1946), Electrochemical Society and NACE, 1949, p. 7.
- Bacon, R. C., Smith, J. J., and Rugg, F. M., "Electrolytic Resistance in Evaluating Protective Merit of Coatings on Metals," <u>Industrial and Engineering Chemistry</u>, vol. 40, January 1948, p. 161.
- 11. BUDOCKS ltr D-410C/mvs dtd 21 April 1954 to Officer-in-Charge NAVCERELAB.

- 12. Young, G. H., Seagren, G. W., and Zehner, J. C., "Antifouling Paints Mechanism of Accelerated Corrosion Under Antifouling Composition Applied to Steel," <u>Industrial and Engineering Chemistry</u>, vol. 37, May 1945, p. 461.
- Cook, F. E., Discussion of "Behavior of Shipbottom Paints Subjected to Cathodic Protection," <u>Corrosion</u>, vol. 9, January 1953, p. 8.
- 14. Hudson, G. A., Brand, B. G., and Mueller, E. G., "An Evaluation of Organic Coatings for the Protection of Domestic Hot-Water Heaters in Conjunction with the Use of Magnesium Anodes,"

  American Chemical Society, Division of Paint, Plastics, and Printing Ink Chemistry, vol. 14, September 1954, p. 98.

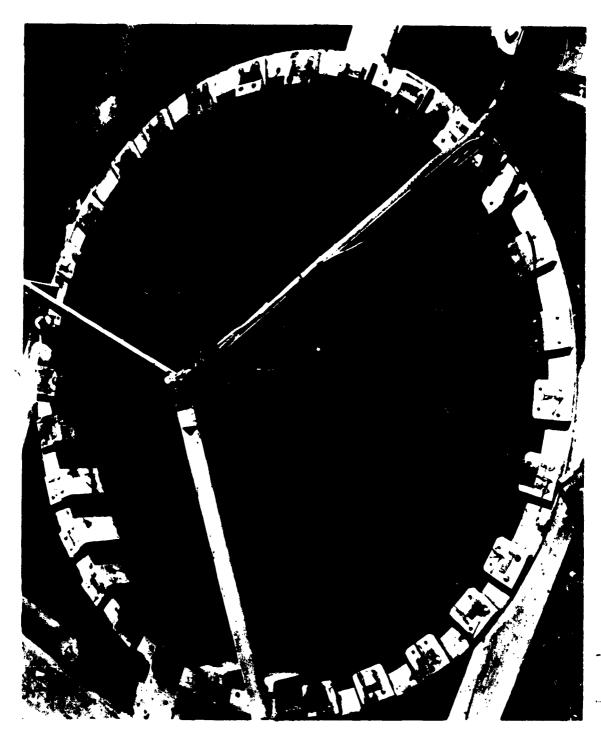


Figure 1. Float used to suspend panels and anode for evaluation of coatings in conjunction with cathodic protection.

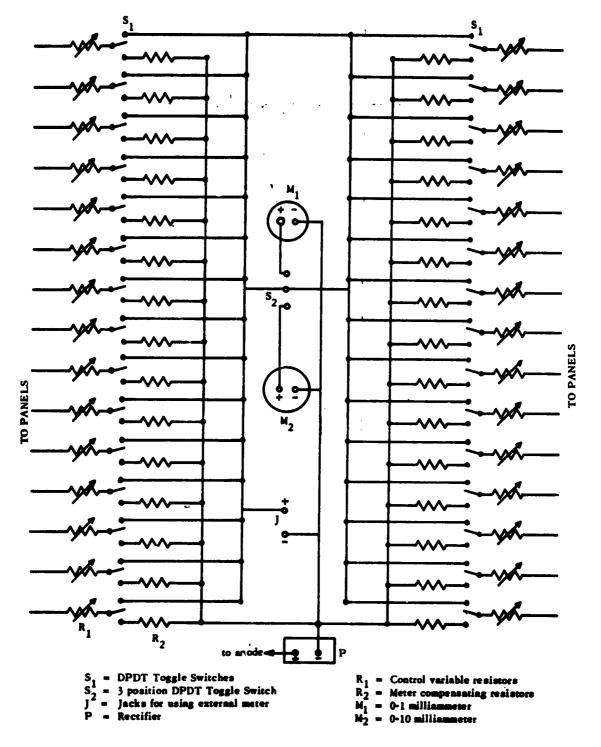


Figure 2. Control system for paint and cathodic protection test.

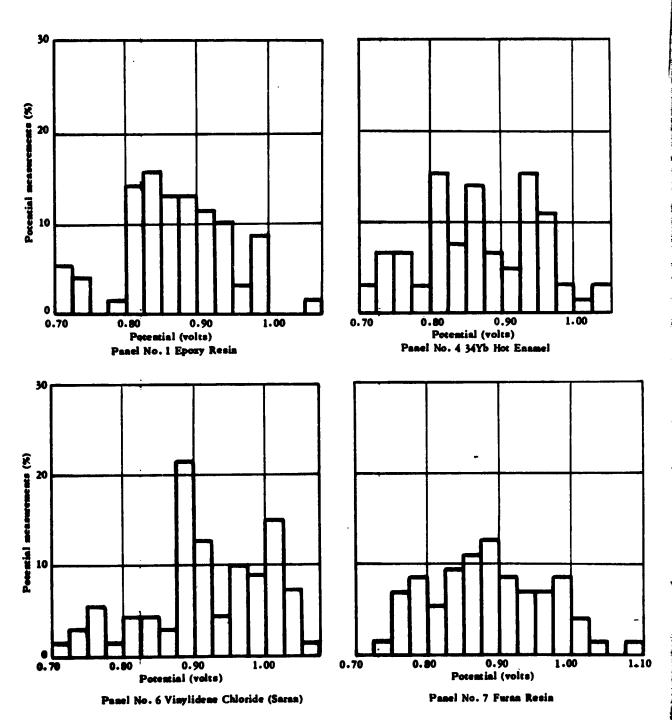


Figure 3a. Potential measurements for the 12-month exposure period.

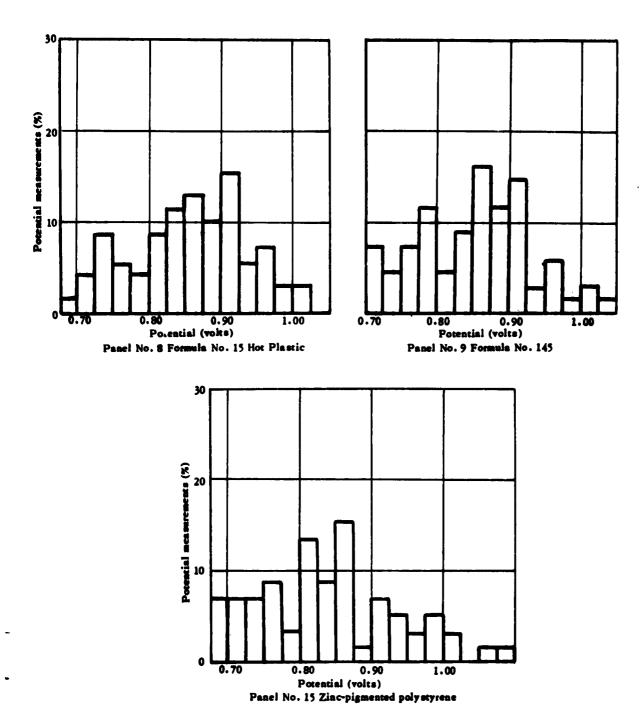


Figure 3b. Potential measurements for the 12-month exposure period.

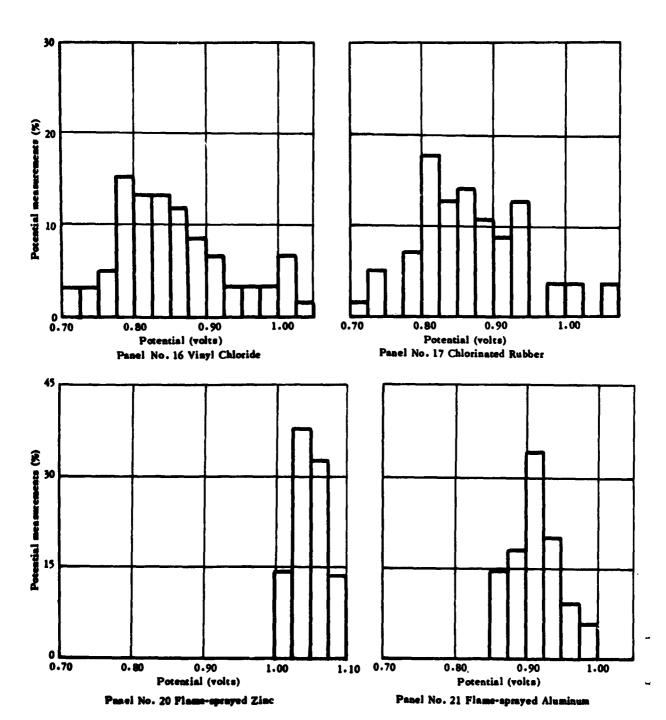
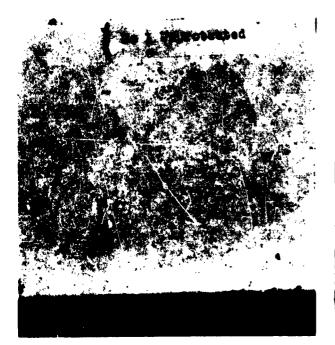


Figure 3c. Potential measurements for the 12-month exposure period.



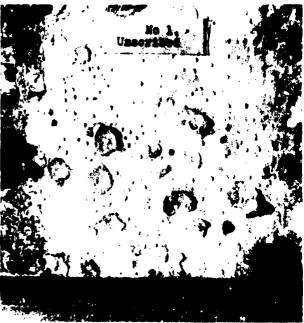




Figure 8. Blistering reaction of epoxy coating with and without cathodic protection.